Microstructure and Fracture Behavior of Structural Ceramic Composites(構造用複合セラミックスの微細組織と破壊挙動)

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論文内容要旨

Chapter 1 Introduction

The objective of the present research which concerns with structural ceramics, is to produce materials having high reliability. To achieve this objective, there are two fundamentally different approaches: flaw control and toughening. The first approach accepts the brittleness of the material and attempts to control the large extreme of processing flaws. The second approach attempts to develop microstructures that impart sufficient fracture resistance leading to a strength insensive to the size of flaws. The former has been a subject of considerable research that identifies the most detrimantal processing flaw, as well as the processing step responsible for those flaws. The toughening approach has emerged more recently. It has the obvious advantage that appreciable processing and post-processing damage can be tolerated without compromising the structural reliability.

The resistance of brittle ceramics to propagation of cracks can be strongly influenced by the microstructure or, in other words, by the use of various reinforcements. In most cases, toughening results in resistance-curve characteristics, wherein the fracture resistance systematically increases with crack extension. The individual mechanisms include: phase transformation, microcracking, crack deflection, crack bridging, etc. They were discussed in detail. In this

chapter, some general concepts about strength and toughness of structural ceramics have been reviewed, with emphasis placed on microstructural control and toughening mechanisms. Then, a microindentation fracture technique coupled with high-resolution electron microscopy was described. Finally, the materials investigated in the present work were introduced.

In this work, I examined both microstructure and fracture behavior of some structural ceramics which have recently attracted attention. They are Al_2O_3-$ZrO_2(Y_2O_3)$ composites, Si_3N_4-SiC-whisker (-SiCw) and -platelet (-SiCp) composites, SiAlON-SiC composites, and Si_3N_4-TiN composites.

Since the mechanical performance of ceramics markedly depends on the size and morphology of the microstructural features as well as interfaces, crystal structures, and internal defects, a strict examination of the microstructure holds a vital role in understanding and developing new materials. In this work, I examind the microstructure of various ceramics from the micrometer to the atomic scale using high-resolution electron microscopy (HREM). On the other hand, besides traditional mechanical testing, a characterization of toughening mechanisms was also attempted by HREM.

Chapter 2 Experimental Procedures

Experimental procedures were described. Preparation of bulk samples and TEM samples, and other tools used in the present work are reviewed. Concerning in particular with the observation of crack paths by HREM, recent studies on whisker-reinforced composites, have demonstrated their importance in understanding the micromechanics of fracture in ceramic composites. Rather than in-situ experiments whose results can be strongly affected by thin-foil effects on the microfracture mode, a crack of appropriate dimensions can be first introduced by a Vickers indentation on a thick sample, from which a thin foil is successively obtained by a back thinning procedure. This method permits to minimize the effect of extraneous phenomena and to observe the original crack extent. Following the back-thinning procedure, the fracture behavior of various composites was examined and toughening mechanisms were discussed. To obtain a complete look-over the crack phenomenon, fracture surfaces were also observed by scanning electron microscopy (SEM).

Chapter 3 Al_2O_3-$ZrO_2(Y_2O_3)$ composites

Microstructure and fracture and deformation behavior of Al_2O_3-24vol%ZrO_2 (0, 2, 3 and 8 mol%Y_2O_3) composites prepared by the pressureless-sintering at 1450℃ using high purity and fine raw powders, were characterized as follows.

The composites were constituted by a homogeneous distribution of Al_2O_3 and ZrO_2 grains with average sizes of 0.5 μm and 0.3 μm, respectively. Most of the ZrO_2 grains in the Al_2O_3-

ZrO_2 (0 %Y_2O_3) have a monoclinic structure (m), but few ones embedded in Al_2O_3 grains are of a tetragonal structure (t). Due to the spontaneous phase transformation of ZrO_2 grains, strong field contrasts were observed in Al_2O_3 near the m- ZrO_2 grains. In Al_2O_3-ZrO_2 (3 % Y_2O_3) and Al_2O_3-ZrO_2 (8 %Y_2O_3), ZrO_2 grains have mainly tetragonal and cubic structures, respectively. The strain field contrast was observed to decrease with increasing Y_2O_3 content. The raw ZrO_2 (0 %Y_2O_3) powders have a monoclinic structure with (100) twin planes, and have a disk-like shape with very fine sizes (about 0.08 μm). In Al_2O_3-ZrO_2 (0 %Y_2O_3), (100) and (302) twins in m-ZrO_2 grains are accompanied by stacking faults and a few of edge dislocations, respectively. Interfaces of these particles have a zig-zag shape with periodic microcracks. Spherical-shaped m-ZrO_2 particles dispersed in the Al_2O_3 matrix have (021) twin, and their terminals have (110) microtwins and a few dislocation exist to accommodate the lattice mismatch without microcracks. By in-situ observation of t- to m-ZrO_2 phase transformation by electron beam irradiation, it was found that a crack propagates along the Al_2O_3/ZrO_2 interface. T-m phase transformation was also observed at the crack tip. In Al_2O_3-ZrO_2 (3 %Y_2O_3), the interface were directly bonded without any impurity, but at some triple points, an amorphous phase was observed. In Al_2O_3-ZrO_2 (8 %Y_2O_3), interfaces and triple points were constituted by a Y-rich amorphous phase. The main fracture mode in Al_2O_3-ZrO_2 (0 %Y_2O_3) was intergranular, but sometimes transgranular fracture was also observed in m-ZrO_2 grains. The main toughening effect in this composite is due to crack deflection along boundaries of fine grains, which have strain fields and microcracks, and due to the plastic deformation in m-ZrO_2 grains. The fracture mode in Al_2O_3-ZrO_2 (3 %Y_2O_3) is a mixed type of intergranular and transgranular fracture. Because phase transformation in t-ZrO_2 grains is partially occurred, it can not give conspicuous contributions on toughening. In Al_2O_3-ZrO_2 (8 %Y_2O_3), cracks propagate both in Al_2O_3 and ZrO_2 grains. However, plastic deformation of cubic-ZrO_2 grains was not observed. Hardness gradually decreased with increasing the temperature up to 1000℃, and then quickly decreased at above 1000℃. The ratio of crack to indentation lengths, (c/a), increased at temperature below 1000℃ and then quickly decreased with increasing the indentation temperature. Fracture mode at 1000℃ was similar to that at room temperature but intergranular fracture at Al_2O_3 and ZrO_2 grainboundaries was frequently observed, and the average crack-length was longer than that at room temperature. This fact may be interpreted by the reduction of strain fields and microcracks at interfaces of Al_2O_3/ZrO_2 by the reverse transformation from t- to m-ZrO_2. In the indentation at 1200℃, cracks were hardly observed, but a strong plastic deformation due to the formation of sub-grains was observed together with grainboundary sliding both in Al_2O_3 and ZrO_2 grains.

Chapter 4 Si_3N_4-SiC-whisker composite

Microstructure and fracture behavior of a SiCw-reinforced composite, fabricated by hot-pressing with Al_2O_3 and Y_2O_3 as sintering additives, were characterized as follows.

Most of the Si_3N_4 grains had an equiaxed-shape with a size of less than 0.3 μm in diameter but, a few elongated grains with an average aspect ratio of about 4 were also observed. SiC whiskers with an aspect ratio of about 5 were homogeneously distributed in the Si_3N_4 matrix. Triple points were constituted by an Y-Al-rich amorphous phase formed during liquid-phase sintering. By high temperature sintering, the α-Si_3N_4 phase of the starting matrix powder transformed to β-Si_3N_4 phase. SiC whiskers were mainly β-typed cubic structure and owned a high density of stacking faults and microtwins. Most of Si_3N_4 grainboundaries and Si_3N_4/SiCw interfaces have a thin amorphous layer. By annealing at 1200℃, amorphous layers were partially crystallized, but thin layers of about 1 nm in thickness still remained amorphous.

The pulling-out behavior of the SiC phase was gradually enhanced with increasing temperature by the existence of the amorphous phase. The main fracture mode at room temperature was an intergranular both along the Si_3N_4 grainboundaries and the Si_3N_4/SiC interfaces. The main fracture mode at 1200℃ was similar to that of room temperature, but lateral cracks were observed at the boundaries between elastic and plastic zones by indentations. When cracks propagated along the Si_3N_4/SiCw interfaces at 1200℃, they propagated along Si_3N_4/amorphous interfaces. The high toughness achieved in this composite was due to a combination of crack deflection, bridging and microcracking mechanisms.

Chapter 5 Si_3N_4-SiC-platelet composites

Microstructure and fracture behavior of hot-isostatically pressed Si_3N_4-SiCp composites, fabricated with different cooling rates, were characterized as follows.

Crystal structures of Si_3N_4 and SiCp in both composites were β-type (h.c.p.), and α-type 4 H and 6 H structures, respectively, independently of the cooling rates. Si_3N_4 grains in the slowly cooled sample, had two patterns, that is, an equixed shape with about 0.3 μm in size and an elongated shape with an aspect ratio of about 5 . In the fastly cooled sample, Si_3N_4 grains showed only the former of the above patterns, and the SiC platelets had high density of partial dislocations terminating on stacking fault planes. The Si_3N_4 grainboundaries and the Si_3N_4-SiCp interfaces in both the samples consisted of a thin amorphous SiO_2 layer with less than 1-2 nm in thickness. F impurity was detected at some triple points. The main fracture mode in the slowly cooled sample was intergranular. In some cases, cracks propagated inside the SiC platelets, along the (001) cleavage plane. Cracks in the fastly cooled sample mostly propagated transgranularly both in the Si_3N_4 grains and the SiC platelets. Some intergranular fracture of SiCp was also observed depending upon its crystallographic orientation. The embrittlement in

the fastly cooled sample was ascribed to residual stress remained at grainboundaries and inside the grains after rapid cooling. On the other hand, high toughness of the slowly cooled samples, which was phenomenologically related to microcracking and crack deflection mechanisms, was determined by bridging and pulling-out of elongated Si_3N_4 grains and SiC platelets.

Chapter 6 SiAlON-SiC composite

Microstructure and fracture behavior of the SiAlON-SiC composite, prepared by pressureless-sintering at 1780℃, were characterized as follows.

In SiAlON- 6 %SiC, nanometer-sized SiC particles were homegeneously dispersed in SiAlON grains and at grainboundaries, accompanied by strong strain contrasts. In SiAlON-12%SiC, most of the SiC particles were located at the grainboundaries and in some ones inside the SiAlON grains. A $Y_5N(SiO_4)_3$ compound was detected by X-ray diffraction. Most of the triple points had a Y and Al-rich amorphous phase. The structure of SiAlON grains was of the β-type h.c.p., and SiC was mainly β-typed cubic but, some grains had an α structure. Most of SiAlON grainboundaries had a random orientation, and contained an amorphous phase on about 1 - 2 nm in thickness, independently on the SiC content. Interfaces between SiAlON and SiC embedded in the SiAlON grains, was directly joined without any amorphous layer. As internal defects, stacking faults and microtwins were observed in the SiC particles, while a few of edge dislocations and stacking faults were observed in the SiAlON grains containing nanometer-sized SiC particles. Vickers hardness and fracture toughness were the highest in the SiAlON- 6 % SiC composites. High temperature hardness decreased with increasing temperature, with a minimum of 1100 at 1200℃. The main fracture mode of the monolithic SiAlON was intergranular, with cracks propagating along the SiAlON grainboundaries with amorphous layer. In SiAlON-6 wt%SiC, fracture modes were a mixed type of intergranular and transgranular both at room temperature and 1200℃. In the cracks propagating in SiAlON grains, short crack bridging occurred by nanometer-sized SiC particles. On the other hand, when a crack propagates along interfaces of SiC particles located at SiAlON grainboundaries, a crack deflection mechanism also contributed on fracture toughening. In SiAlON-12wt%SiC, cracks more straightly propagate in the SiAlON grains and submicron-sized SiC particles, and the main fracture more transgranular.

Chapter 7 Si_3N_4-TiN composite

Microstructure and fracture behavior of the CVD Si_3N_4-TiN composite are characterized as follows.

Si_3N_4 grains had a columnar structure parallel to their growth direction, with grain sizes of about 8 μm. TiN fibers were homogeneously distributed in the Si_3N_4 matrix and their axes

were parallel to the [001] direction of Si_3N_4. Most of their cross sections had an ellipsoidal shape of about 15nm in diameter. Most of the Si_3N_4 have a β-typed hexagonal structure, but sometimes a α-typed trigonal structure, and TiN fibers have a NaCl-type structure. Grainboundaries and interfaces show direct bonding without any impurity phase. The main fracture mode was a mixed type of intergranular and transgranular fracture. Main fracture toughening mechanisms were crack bridging and microcracking by the dispersed TiN fibers in Si_3N_4.

Chapter 8 Summaary

In this chapter, the results of microstructure and fracture behavior of the above listed composites were individually summarized. Furthermore, the general relationships between microstructure and fracture behavior were discussed in some details.

審 査 結 果 の 要 旨

近年，構造用セラミックスの破壊靭性値を高めるために，微細組織の制御を基本とした種々の複合化が計られている。本研究は，これら材料の高靭化機構の基礎的知見を得ることを目的として，５つの複合セラミックスの微細組織と破壊挙動の詳細な研究を行ったもので，全編８章よりなる。

第１章は序論であり，本研究の背景と目的を述べている。

第２章は，本研究で用いた複合セラミックスの作製条件，微細組織およびクラック伝播の観察法，機械的性質の測定法，について述べている。

第３章では Al_2O_3-ZrO_2 複合セラミックスを調べ，単斜晶系をとる ZrO_2 結晶粒内の塑性変形が破壊靭性に大きな寄与していることを初めて見いだした。また，1200℃の高温の変形において，Al_2O_3 および ZrO_3 粒内に生成した亜粒界のすべりによって塑性変形が行っていることを見いだした。

第４章では SiC 繊維で強化した Si_3N_4 複合セラミックスを調べ，長く伸びた Si_3N_4 および SiC 結晶粒によるクラックの大きな偏向および微小クラックの発生を観察し，それらがクラック伝播エネルギーを吸収して破壊靭性を高めていることを明らかにした。

第５章では板状 SiC で強化した Si_3N_4 複合セラミックスを調べ，焼結後の熱処理の違いによる破壊靭性値の低下は，クラック伝播が粒界から粒内へ変化するためであると明らかにした。高い破壊靭性値を示す材料では，粒界を伝播するクラックの偏向および主クラック近傍における微小クラックの発生を観察した。

第６章では SiAlON-SiC 複合セラミックスを調べ，SiAlON 粒内に分散する微小な SiC がクラックのブリッジング現象を起こしていることを見いだした。

第７章では化学気相析出法で作製された Si_3N_4-TiN 複合セラミックスを調べ，大きな Si_3N_4 結晶粒内に分散した TiN 繊維とクラック先端との強い相互作用を見いだし，クラックブリッジリングと微小クラックの発生による高靭化機構を明らかにした。

第８章は総括で，本研究の結果から，微細組織の制御によって，構造用複合セラミックスの破壊靭性値を高めるための種々の因子を議論している。

以上要するに本論文は，構造用複合セラミックスの微細組織と破壊挙動との詳細な研究から，高靭化機構の基礎的な知見を得たもので，材料物性学の発展に寄与するところが少なくない。

よって，本論文は博士（工学）の学位論文として合格と認める。